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13. ABSTRACT (Maximum 200 words) During this project we have studied the magnetic behavior of Ni, V, Rh, Gd, and Mn Clusters, interaction of metal clusters with substrates and hydrogen, iron-carbon clusters, the hydrogen-vacancy complexes and have explained anomalies spectroscopic data on metal cluster anions. Our studies have enabled (1) an understanding of the magnetic behavior of clusters of conventional ferromagnetic metals Fe, Co, Ni, (2) predicted ferromagnetism in Rh <sub>n</sub> clusters, (3) examined spin canting in Gd <sub>n</sub> clusters and (4) predicted that clusters of antiferromagnetic solids like Mn are magnetic. We have offered the first explanation of the anomalies in the negative ion spectroscopy of Li <sub>n</sub> clusters and have provided a basic understanding of the Hydrogen-vacancy complexes.				
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**(2). Personnel Supported**

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S. N. Khanna (summer)  
B. K. Rao (summer)  
C. Ashman (graduate student)  
B. Martin (part-time assistant)

**(3). Inventions**

**None**

#### (4) Scientific Progress and Accomplishments.

It is difficult to describe, even briefly, all the work we have done during the tenure of this grant as we have published 34 papers during this period. In the following, we provide an outline of the salient features of our work and refer the reader to the original papers for details.

##### (i) Magnetism of Ni, V, Rh, and Gd clusters

Using a combination of classical molecular dynamics simulation and first principles molecular orbital theory, we provided the first comprehensive study of the equilibrium geometries, energetics, electronic structure, vertical ionization potential, and magnetic properties of Ni clusters containing up to 21 atoms. The molecular dynamics simulation made use of a tight binding many body potential while the calculations based on molecular orbital theory were carried out self-consistently using the numerical atomic bases and the density functional theory. The adequacy of the molecular dynamics results for the energetics and equilibrium geometries was first established by comparing the results with those obtained from the self-consistent molecular orbital theory for clusters of up to six atoms. For larger clusters, equilibrium geometries were obtained from molecular dynamics simulation and their electronic structure and properties were calculated using molecular orbital theory without further geometry reoptimization. Frozen core and local spin density approximations were used in the molecular orbital calculations. In small clusters ( $n \leq 6$ ), the calculations were repeated by including the effect of all electrons and the gradient correction to the exchange-correlation potential. We showed that the clusters do not mimic the bulk structure and undergo significant geometrical changes with size. The binding energy per atom, on the other hand, increases monotonically with size. The evolution of the geometries is found to be correlated with the underlying changes in the nature of bonding. The calculated geometries as well as the vertical ionization potentials and magnetic moments of Ni clusters were compared critically with recent experimental data. Limitations in both theory and experiment were pointed out and a case was made for a better understanding of the role of temperature.

The calculations also revealed the existence of two nearly degenerate isomeric forms of  $Ni_7$  - a capped octahedron and a pentagonal bipyramid. These isomers have different magnetic moments and they react differently with  $N_2$ . The existence of isomers solved a longstanding discrepancy between the calculated geometry and that inferred from the experimental reactivity data. The limitations of current experiments in identifying existence of isomers was pointed out. An in depth study of the ground state geometry of  $Ni_{13}$  led to the conclusion that its geometry is a Jahn-Teller distorted  $D_{3d}$  icosahedron. Its effect on magnetic properties was also discussed.

Thermal stabilities and dynamics of small Nickel clusters consisting of 7 to 23 atoms were studied extensively by molecular dynamics (MD) method. Physical properties such as caloric curve, melting temperature, and bond length fluctuations were computed. The simulation indicated that the clusters undergo solid  $\rightleftharpoons$  liquid phase change with the increase in internal energy. The melting temperatures were found to be non-monotonic function of cluster size with some clusters exhibiting pre-melting behavior. Considerable depression in the melting point of small clusters was observed and the highest melting temperature for small clusters was found to be almost half the value in bulk nickel. The results were discussed in the light of recent nanocalorimetric experiments on small finite particles.

Following our initial prediction that  $Rh_{13}$  cluster could be magnetic, Stern-Gerlach experiments were carried out by Bloomfield and co-workers. In addition to verifying our prediction, Bloomfield *et al.* found that  $Rh_n$  clusters up to  $n=80$  are ferromagnetic. Although several calculations on a small number of Rh clusters have been performed since then, we are the first group to have studied systematically the global equilibrium geometries and the corresponding electronic structure and magnetic moments of  $Rh_n$  clusters up to  $n=14$ . We have used a combination of molecular dynamics and first principles method for these calculations as described for Ni clusters previously. We not only explain the strong size dependence of the magnetic moment, but also unravel the striking relationship among isomers, magnetism, and reactivity. We were able to demonstrate that



the magnetism of Rh clusters can be changed by modifying their structure through chemical reaction, thus linking the field of magnetism and catalysis of atomically engineered materials.

Despite the progress made in understanding the magnetism of transition metal clusters, the magnetism of rare-earth clusters has remained an unsolved problem. In contrast to transition metal clusters where magnetism was found to be enhanced, the measured moments in Gd clusters range between 0.5 - 3.0  $\mu_B$  per atom, far below the bulk value of 7.55  $\mu_B$ /atom. The moments were also found to increase with temperature. We have examined the structure and spin configuration of a Gd<sub>13</sub> cluster using theoretical electronic structure calculations and a Heisenberg model. The structure calculations show that the ground state geometry of the cluster has an hcp arrangement with a slightly reduced nearest-neighbor distance compared to bulk and an atomic moment of 7.8  $\mu_B$ /atom. The spin configuration was calculated using the Heisenberg model with a RKKY-like interaction. The effects of competing ferromagnetic and antiferromagnetic coupling for the nearest- and next-nearest-neighbor interaction, respectively, was investigated. We showed that for a range of interaction strengths the spins assume a canted configuration. This effect leads to lower net magnetization of the cluster, and accounts for the anomalous low moments of Gd<sub>n</sub> clusters which have been experimentally observed. A similar model has recently been used to understand the alignment between the surface and bulk moments.

#### (ii) Interaction of metal clusters with substrates and hydrogen

Magnetic properties of free and supported Vanadium clusters of up to four atoms were calculated self-consistently using the density functional theory. Both free and supported V<sub>n</sub> clusters on Cu(001) and Ag(001) are found to be magnetic, although the magnetic moments depend strongly on the cluster size. While free clusters have ferromagnetic ground states, the supported V clusters in general prefer antiferromagnetic configurations. The role of inter-atomic distances, coordination, and surface morphology on the magnetic properties of V clusters were discussed. To understand the effect of substrate relaxation on the magnetic moment of supported clusters, we studied V<sub>2</sub> on Cu(001) using a cluster model where Cu(001) was represented by 20 atoms. For the unrelaxed surface, the V sites were found to have a large magnetic moment as predicted by previous studies. The surface Cu atoms, however, were found to undergo significant relaxations and the V-V distance at the surface is close to that of an isolated V<sub>2</sub> molecule. These relaxations quench the magnetic moments at the V sites demonstrating the importance of substrate relaxation on magnetism of supported clusters.

We were the first group to study the magic numbers of Ag<sub>n</sub> clusters on Ag(001) surfaces by using molecular dynamics simulation. We demonstrated the importance of substrate geometry on cluster stability and showed that magic numbers of two dimensional clusters are different from those in three dimension. This finding complements the recent experimental observation. The energetics for various magnetic configurations of Mn<sub>n</sub> clusters (n = 1,2,3,9) on Ag (001) substrate were calculated from first principles using the KKR method. Our results show that the magnetic moment/atom of supported Mn clusters is very close to their free-atom value of 5 $\mu_B$ . This prediction has now been verified experimentally. In addition, the clusters also exhibit magnetic bistability making it possible to probe quantum tunneling in mesoscopic systems.

Interaction of H<sub>2</sub> and He clusters with neutral and cationic atoms of Al, Ni, Cu, Co were studied. The bonding mechanism between the gas molecules and metal atoms was shown to depend on the charge state of the metal atom. H<sub>2</sub> dissociates and binds atomically with neutral metal atoms while a large number of H<sub>2</sub> molecules in molecular form can be attached to a metal ion. This effect, brought about by polarization of the H<sub>2</sub> molecules, was studied for the first time by our group using quantum chemical procedure.

#### (iii) Iron-Carbon Clusters

In the bulk phase, carbon-transition metal systems form very stable carbides with rather high melting temperatures. However, in clusters the composition of carbon and transition metal atoms that exhibit unusual stability is not always the same as what one finds in the bulk phase. For example, clusters with the composition X<sub>8</sub>C<sub>12</sub> (X = Ti, V, Cr, Fe, Mo, Zr, Hf) have been found to be very stable and are now known as "met-

cars". The iron-carbon system, however, does not exhibit any unusual stability at the 8-12 composition. This anomaly has prompted a number of experimental studies of  $\text{Fe}_x\text{C}_y$  clusters. Using different levels of theory based on quantum chemical and density functional methods (with local spin density and gradient approximations), we studied the equilibrium geometries, total energies, and electronic structure of  $\text{FeC}_n$  ( $n \leq 3$ ) clusters. All levels of theory yielded the structures to be cyclic - consistent with the experimental observation. The binding energies, bond lengths, and Mulliken charges obtained from these were found to be in agreement, establishing the reliability of the local spin density approximation in studying metal-carbon clusters. We also showed that  $\text{C}_n^-$  ( $n \leq 7$ ) clusters are all linear chains, and that  $\text{C}_n^-$  clusters for  $n \leq 7$  are unstable. Our calculations provided a quantitative account of the experimental data.

#### (iv) Hydrogen-vacancy Complexes in Ni

Study of metal-hydrogen systems is important to hydrogen storage technology. Fukai and Okuma carried out an in situ x-ray-diffraction study of Ni and Pd under high pressure ( $\sim 5$  GPa) and high temperature ( $\sim 800^\circ\text{C}$ ). They observed an anomalous lattice contraction amounting to  $\sim 0.5 \text{ \AA}^3$  per metal atom in the hydride phase. This contraction remained even after hydrogen was removed by heating the sample to  $400^\circ\text{C}$ , but was annealed out at  $800^\circ\text{C}$ . They attributed this lattice contraction to the copious amount of vacancy formation ( $\sim 20\%$ ) induced by the presence of hydrogen.

Using a self-consistent cluster-embedding (SCCE) scheme, we have calculated the electronic structure, energetics, and magnetic moments of pure Ni and Ni containing vacancies as well as vacancy-hydrogen complexes. A comparison of our results on the 3d-band width, the magnetic moment, and cohesive energies in pure Ni with experiment leads us to believe that the SCCE method can be successfully applied to study properties of crystalline materials.

We then used this method to study the binding energies of hydrogen atoms to vacancies and the preferred location inside the vacancies. We found that a single hydrogen atom would not preferentially locate at the center of a vacancy. The equilibrium location of six hydrogen atoms is along the octahedral directions displaced by  $a_0/2$  ( $a_0$  being the lattice constant) from the vacancy center. This is similar to the positions of oxygen in NiO. The binding energy of the six hydrogen atoms inside the vacancy exceeds that of the  $3\text{H}_2$  molecules, confirming the stability of such a complex. In addition, this gain in energy is larger than the vacancy formation energy. Thus hydrogen can induce spontaneous vacancy formation as suggested by the experiment of Fukai and Okuma and earlier results of Meyers *et al.* based on the effective-medium theory.

The electronic structure and magnetic properties of the vacancy-hydrogen complex in Ni is also very interesting. As hydrogen atoms move away from the vacancy center, the magnetic moments of the nearest Ni atom continually decrease, and as the hydrogen atoms reach their equilibrium configuration, the magnetic moment couples antiferromagnetically to the lattice. This prediction should be verifiable in the hydride phase.

#### (v) Anomalous Spectroscopy of Metal Cluster Anions

A recent experiment on the photoelectron spectra of  $\text{Li}_4^-$  by Sarkas *et al.* suggests that Li clusters, as is the case with crystals, may not behave the same way as other alkali metals do. These authors had earlier observed that the photoelectron spectra of  $\text{Na}_4^-$  and  $\text{K}_4^-$  were similar and were both characterized by two broad peaks separated in energy by about 0.5 eV. In contrast, the photo detachment spectra of  $\text{Li}_4^-$  are characterized by two very sharp peaks separated by an energy gap of about 0.1 eV. To understand the origin of this anomalous behavior, we have carried out self-consistent calculations of the equilibrium geometry, binding energy, and electronic structure of  $\text{Li}_4^-$  and  $\text{Na}_4^-$  clusters. We were the first to demonstrate that, while the ground state of  $\text{Na}_4^-$  is a spin doublet linear chain, the ground state of  $\text{Li}_4^-$  consists of two nearly degenerate isomers having spin doublet rhombus and spin quartet tetrahedral configurations. The existence of these isomers is responsible for the anomalous photoelectron spectra of  $\text{Li}_4^-$ . It is argued that a comparison between theory and experiment of photoelectron spectroscopy can not only give information regarding the cluster geometry but also its isomers and spin multiplicities. We have also shown that unusual properties of  $\text{Li}_4^-$  are rooted in the electronic structure of the atom itself. Experiments designed to detect the possible existence of

a high spin  $\text{Li}_4^-$  state were suggested. These calculations have since been repeated by other authors who have agreed with our conclusions. We have also carried out the first theoretical calculation of the photo detachment spectroscopy of Ni cluster anions. The anomalous spectra of  $\text{Ni}_2^-$  and  $\text{Ni}_3^-$  were attributed to the existence of isomers.

(vi) Ferromagnetism in  $\text{Mn}_n$  Clusters :

Unlike any other transition metal clusters, and in sharp contrast to bulk behavior, Mn clusters containing up to 5 atoms are found to retain their atomic magnetic moments.  $\text{Mn}_2$ ,  $\text{Mn}_3$ ,  $\text{Mn}_4$ ,  $\text{Mn}_5$  clusters in their ground states are coupled ferromagnetically and carry moments of 10, 15, 20 and 25  $\mu_B$ , respectively. We have also identified several low lying excited states. These results are based on all electron first principles self consistent calculations using density functional theory and generalized gradient approximation. Predictive capability of this approach is established by comparing the calculated energetics, electronic and magnetic properties of  $\text{Mn}_2^+$  with experiment.



(5) Technology Transfer : None